



Master of Science in Mechanical Engineering

Swelling kinetics of constrained hydrogel spheres

구조적 제약이 있는 하이드로젤 구의 팽윤 동역학

August 2023

Graduate School of Mechanical Engineering Seoul National University

Théotime Cano

Swelling kinetics of constrained hydrogel spheres

Advisor Ho-Young Kim

Submitting a master's thesis of Mechanical Engineering

April 2023

Graduate School of Mechanical Engineering Seoul National University

Théotime Cano

Confirming the master's thesis written by Théotime Cano

June 2023

Chair	송성진_	(Signature)
Vice Chair	김호영_	(Signature)
Examiner	박형민_	(Signature)

Abstract

A cross-linked polymer network immersed in a solvent will absorb molecules from its surroundings, leading to transient swelling. The entropy-driven mixing behavior makes the solvent molecules flow in the network and fill its pores, increasing the pore pressure. The network is then stretched, increasing the pores' size and allowing for more solvent to flow inward. The permeability of the gel should increase with the pores' size, affecting the kinetics of the swelling process. When an equilibrium is reached between the energetically-favorable mixing and the energeticallyunfavorable stretching, the swelling stops. Under the constraint of a semipermeable membrane, the system will swell less and grow a larger internal pressure in return. No theoretical analysis of the constrained growth has existed so far. We use a nonlinear poroelastic theory to model the kinetics of swelling under constraint and find the simulation results agree well with our experimental data from hydrogel beads made of a mixture of 3sulfopropyl acrylate potassium salt and acrylamide, bathed in water. Understanding and predicting the response time and the actuation stress developed during the swelling of constrained hydrogels help the design of polymer-based soft actuators.

Keyword : Hydrogel, membrane, swelling, hyperlinear, kinetics **Student Number :** 2021-22015

i

Table of Contents

Chapter 1. Introduction 1		
1.1. Study Background 1		
1.2. Purpose of Research		
Chapter 2. Overview of the theory 7		
2.1. Geometry		
2.2. Free energy density		
2.3. Stress tensor and chemical potential		
2.4. Kinetic law1 1		
Chapter 3. Simulation 1 4		
3.1. Numerical scheme1 4		
3.2. Explanation of the process1 8		
Chapter 4. Materials and method 3 1		
4.1. Materials		
4.2. Fabrication of the hydrogel		
4.3. Tensile tests		
4.4. Compressive tests		
4.5. Swelling rate measurement		
4.6. Validation		
Conclusion 4 3		
Bibliography 4		
Abstract in Korean 4 6		

Chapter 1. Introduction

1.1. Study Background

A three-dimensional polymer network can be created by cross-linking long polymers. Immersed in a solvent, this network may absorb molecules from its surroundings, thus creating a mixture called polymer gel. If the solvent is water, it is referred to as a hydrogel. Bathed in a solvent and under no external constraint, the gel will swell by absorbing new solvent molecules until it reaches equilibrium. Gels are widely used in micromechanical systems as autonomous flow controllers⁽¹⁾, pH sensors⁽²⁾ or actuators⁽³⁾; in biology for injury repair⁽⁴⁾ or as carriers for drug delivery⁽⁵⁾ and in soft robotic stimuli-responsive muscle-like systems⁽⁶⁾. as They are biocompatible, similar to living tissues and adjustable in shapes and chemical properties⁽⁷⁾. Their major flaw, namely their slow response time, can be enhanced using electro-osmosis⁽³⁾, for example.

Historically, one of the first attempts to model the kinetics of swelling of

hydrogels was conducted by Tanaka *et al.*⁽⁸⁻⁹⁾, using constitutive equations from linear elasticity and modelling only the polymer network, not the fluid flowing inside it. This framework has been subject to some criticisms⁽¹⁰⁾, mainly due to its lack of physical foundations and its bold assumption of small deformations. Furthermore, this theory is unable to predict complex behaviors of hydrogels such as pH-driven phase transition. Hence, Hong *et al.*⁽¹¹⁾ proposed a hyperlinear theory for elastomers. From a thermodynamic point of view, two processes are dominant in the energetic balance of the swelling. The absorption of water molecules makes the hydrogel swell and the polymer network is stretched in return. When an energetic equilibrium is reached between the energeticallyfavorable absorption and the energetically-unfavorable stretching, the swelling stops. An important aspect of hydrogels is that, as they swell, their pores expand. Hence, as the size of the pores is used to characterize the permeability, it should increase throughout the process, drastically affecting the dynamics of the swelling. Hong et al. built a theory for large

deformations using a thermodynamic approach, based on the works of Flory⁽¹²⁾ for the mixing part, Huggins⁽¹³⁾ for the stretching part and Grattoni⁽¹⁴⁾ for the deformation-dependent permeability, among others.

1.2. Purpose of Research

This study aims at analyzing the kinetics of the constrained swelling of a hydrogel wrapped by a relatively stiff membrane. When absorbing new water molecules through the membrane, the wrapped hydrogel will only swell slightly due to the constraint by the membrane and an important internal pressure will develop⁽³⁾. First, we will tackle the problem of the kinetics of free swelling, that is to say the swelling of the hydrogel without the membrane. Then, we will consider the same question with a wrapped hydrogel. On the one hand, the addition of a membrane leads to a smaller final swelling ratio. On the other hand, an important internal pressure driven by the osmotic mixing potential of the polymer will grow, which can be of interest in many applications of soft actuators

In the following, the first part will be devoted to the theoretical analysis. Then, further insights of the internal behaviour during the swelling process will be presented through simulations. The experimental setup will be presented and the simulated results will be compared with experimental data.



Fig. 1 Sample of swelling experiments for the free case. Pictures are taken at logarithmically-spaced time intervals (3.9 min, 7.8 min, 16 min, 39 min, 1.6h, 3.4h, 7.6h and 17h, respectively) and from a top view. Surface instabilities, which we neglected in this study, can be seen in the beginning of the experiments. Each grid measures 5 mm.



Fig. 2 Sample of swelling experiments for the constrained case. Pictures are taken at logarithmically-spaced time (8.7 min, 17 min, 52 min, 1.4h, 2.6h, 4.6h, 8.2h and 15h, respectively) intervals and from a top view. Surface instabilities, which we neglected in this study, can be seen in the beginning of the experiments. Each grid measures 5 mm.



Fig. 3 Schematics of the inhibition process. The mixture swells because of the absorption of new solvent molecules which fill and expand the pores of the polymer network. In the constrained case, the gel swells less than in the free case.

Chapter 2. Overview of the theory

This section is a combination of the theoretical frameworks proposed by Engelsberg *et al.*⁽¹⁵⁾ and Bertrand *et al.*⁽¹⁶⁾, which themselves are based on the fundamental work of Hong *et al.*⁽¹¹⁾.

2.1. Geometry

We consider the problem of the swelling of a hydrogel sphere, first freely swelling in pure water and then constrained by a membrane. Let's consider a spherical sphere of initial radius a, the dry state being our reference state. If $\vec{R} = R\vec{e}_r$ is the position vector in the reference state and $\vec{r} = r(R,t)\vec{e}_r$ is the position vector in the current state at time t, we define the eigenvalues of the deformation tensor $F = \partial \vec{r} / \partial \vec{R}$, which are the stretches in the three principal directions, as:

$$\lambda_r = \partial r / \partial R$$
, $\lambda_\theta = \lambda_\Phi = r / R$,

and the Jacobian determinant, which is the swelling ratio, as:

$$J = \det(F) = \lambda_r \lambda_\theta \lambda_\phi = \lambda_r \lambda_\theta^2 = 1/\varphi,$$

where φ is the volume fraction of polymer in the mixture.

2.2. Free energy density

The basic assumption of the ideal elastomeric gel theory is that the mixing and the stretching part can be totally separated in the computation of the free energy density W. The stretching part will only depend on the three eigenvalues of the deformation tensor F, and the mixing part will only depend on the number of additional water molecules per unit volume of dry polymer C:

$$W = W_{stretch}(F) + W_{mix}(C) + p(1 + \Omega C - \det(F)),$$

where we further added a microscopic incompressibility condition using a Lagrangian multiplier p, which states that the increasing in volume of the system can only be due to absorption of additional solvent molecules of individual volume Ω .

 $W_{stretc\hbar}$ models the elastic contribution to the free energy of an arbitrarily deformed network of cross-linked polymers, ignoring the influence of the

fluid on the network. The term is usually derived using a Gaussian-chain elastic model, which yields

$$W_{stretc\hbar} = \frac{Nk_BT}{2} \left[\lambda_r^2 + \lambda_{\theta}^2 + \lambda_{\phi}^2 - 3 - 2\ln(\lambda_r \lambda_{\theta} \lambda_{\phi}) \right],$$

where N is the number of chains per unit volume of dry polymer, k_B is the Boltzmann constant and T is the temperature.

 W_{mix} models the contribution to the free energy of the mixing of polymers and water molecules, ignoring the elastic response of the polymer network. The term is usually derived from the Flory-Huggins lattice theory, which yields

$$W_{mix} = \frac{k_B T}{\Omega \varphi} \Big[(1 - \varphi) \ln(1 - \varphi) + \frac{\varphi}{\alpha} \ln(\varphi) \\ + \chi \varphi (1 - \varphi) \Big],$$

where α is the ratio of the volume of a polymer molecule to that of a solvent molecule and the constant χ is called the Flory-Huggins interaction parameter, or simply the mixing parameter. The first two terms are entropic in nature and the term containing χ is enthalpic. If $\chi < 0$ the enthalpic contribution of the mixing is energetically favorable, but it is not if $\chi > 0$.

2.3. Stress tensor and chemical potential

From there we can compute the true stress as

$$\sigma_{i} = \frac{\lambda_{i}}{J} \left(\frac{\partial W}{\partial \lambda_{i}} \right)_{T,C,\lambda_{j}} \text{ wit } \hbar \text{ } j \neq i,$$

and the chemical potential as

$$\mu = \left(\frac{\partial W}{\partial C}\right)_{T,\lambda_i} \text{ for all } i.$$

The elastic contribution to the true stress, $\sigma'_{i'}$ and the Lagrange multiplier which can be interpreted as the pore pressure, p, thus relate to the total stress following the usual form of Biot's theory of poroelasticity: $\sigma_i = \sigma'_i - p$. Similarly, the chemical potential is interpreted as the sum of the osmotic pressure, Π , being the mixing contribution, and the pore pressure, p, being the mechanical contribution: $\mu/\Omega = \Pi + p$. This yields

$$\sigma_i = Nk_BT\left(\frac{\lambda_i^2 - 1}{J}\right) - p,$$

$$\frac{\mu}{\Omega} = \frac{k_B T}{\Omega} \left[ln \left(\frac{J-1}{J} \right) + \frac{1-1/\alpha}{J} + \frac{\chi}{J^2} \right] + p.$$

2.4. Kinetic law

We consider a model where the kinetic behavior of water molecules in the gel is driven by the gradient of chemical potential. The flux of water molecules assumes the form of Darcy law with a deformation-dependent permeability which accounts for the fact that the mean cross section of the pores of the polymer network should increase with the swelling. The conservation of water molecules yields

$$\frac{\partial C}{\partial t} + \nabla_R \cdot \vec{j}_R = 0,$$

with \vec{j}_R the nominal flux of water molecules and the divergence being taken with respects to the coordinate in the reference state. The true deformation-dependent Darcy's law (with \vec{j}_r the true flux of solvent) is

$$\vec{J}_r = -\frac{cD(J)}{k_B T} \nabla_r \mu,$$

where c = C/J is the true concentration of water molecules. The deformation-dependent permeability takes the usual form derived from Gratonni's work:

$$D(J) = D_0 \frac{J-1}{J} J^\beta,$$

where the permeability parameter D_0 will be used as a fitting parameter and $\beta = 1.5$ is fixed according to the literature. We consider a situation with no external volumetric forces. Thus, the mechanical equilibrium requires that $\nabla_r \cdot \sigma = 0$.

We can now wrap everything up and proceed to non-dimensionalize the governing equation, introducing the non-dimensionalized variables $\rho = R/a$ and $\tau = Dt/a^2$. Note that the value of the effective permeability D(J) will be different for the two cases: D should be smaller in the constrained case than in the free case. That being said, we can derive the final governing equation:

$$\begin{split} \frac{\partial J}{\partial \tau} &= \frac{1}{\rho^2} \frac{\partial}{\partial \rho} \left(\rho^2 (J-1) J^{\beta-1} \left\{ \frac{\lambda_{\theta}^4}{J^4} \left[1 + \frac{J-1}{\alpha} - 2\chi \frac{J-1}{J} + N \Omega (J-1) \left(1 + \frac{J^2}{\lambda_{\theta}^4} \right) \right] \frac{\partial J}{\partial \rho} \right. \\ &+ \frac{2N \Omega J - 1}{\rho} \left(\frac{J^2}{\lambda_{\theta}^3} - \lambda_{\theta}^3 \right) - \frac{4N \Omega J - 1}{\lambda_{\theta}} \frac{\partial \lambda_{\theta}}{J} \right) , \end{split}$$

with the last closing condition

$$\lambda_{\theta} = \frac{1}{\rho} \left[\int_{0}^{\rho} 3x^{2} J\left(x,\tau\right) dx \right]^{1/3}.$$

We want the boundary of the gel to be in equilibrium with the surrounding

fluid, namely pure water, so that the chemical potential on the boundary

 μ_b is expressed as

$$\mu_b = \Pi + \frac{Nk_B T \Omega}{J} \left(\frac{J^2}{\lambda_{\theta}^4} - 1 \right) + 2G_m \frac{\hbar}{a} \Omega \left(\lambda_{\theta}^2 - \lambda_{\theta}^{-4} \right) = 0,$$

where G_m is the shear modulus of the membrane and h is its thickness. The radial stress-radial stretch relation is computed for the case of an incompressible Neo-Hookean thin shell. Finally, the condition of no flux of solvent molecules at the center of the sphere is satisfied by imposing

$$\left(\partial\lambda_{\theta}/\partial\rho\right)\left(\rho=0,\tau\right)=\left(\partial J/\partial\rho\right)\left(\rho=0,\tau\right)=0.$$

Chapter 3. Simulation

3.1. Numerical scheme

To integrate the governing equation, we use the Crank-Nicolson discretization method for the temporal derivative with a first-order finite difference discretization scheme for the spatial derivative. This method being semi-implicit and the governing equation being non-linear, we solve the problem by, at each time step, computing the values of J and λ_{θ} at every spatial step at once, using the Newton-Raphson's method to find the root of the residue function.



Fig. 4 Radius over initial radius λ_{θ} against the non-dimensionalized radius ρ , at various time steps for the free (in blue) and the constrained (in red) cases.



Fig. 5 Fluid volume fraction φ_f against the non dimensionalized radius ρ , at various time steps for the free (in blue) and the constrained (in red) cases.



Fig. 6 Normalized chemical potential $\mu/(\Omega N k_B T)$ against the nondimensionalized radius ρ , at various time steps for the free (in blue) and the constrained (in red) cases.

3.2. Explanation of the process

The governing equation is then integrated to understand in more depth the swelling process in both cases. We proceed to plot several variables against the non-dimensionalized radius ρ ($\rho = 0$ refers to the center of the sphere and $\rho = 1$ to its boundary, at all time). We plot them for both the free and the most constrained case of our experiments, at different time steps, logarithmically spaced between t = 0 h and $t \simeq 20$ h. Parameters used in this simulation are either fixed, computed from experiments or fitted to experimental data.



Fig. 7 Elastic radial stress σ'_r against the non-dimensionalized radius ρ , at various time steps for the free (in blue) and the constrained (in red) cases.



Fig. 8 Elastic azimuthal stress σ'_{θ} against the non-dimensionalized radius ρ , at various time steps for the free (in blue) and the constrained (in red) cases.



Fig. 9 Pore pressure p against the non-dimensionalized radius ρ , at various time steps for the free (in blue) and the constrained (in red) cases.



Fig. 10 Normalized osmotic pressure $\Pi/(Nk_BT)$ against the nondimensionalized radius ρ , at various time steps for the free (in blue) and the constrained (in red) cases.

Figs.4-5-6 show that the hydrogel swells from its boundary to its center, solvent diffusion being driven by the chemical potential gradient. The gel's radius increases by a factor slightly larger than three in the free case and by a factor slightly lower than two in the constrained case (Fig.4). The final state in the free case is almost fully swollen with a final value of the fluid volume fraction $\varphi_f \simeq 0.97$ while $\varphi_f \simeq 0.74$ in the constrained case, showing the non-negligible presence of polymers in the final mixture (Fig.5). The chemical potential rises until it reaches a value of equilibrium almost equal to that of the solvent in the case of high swelling ratio, and lower than the said value in the constrained case to account for the nonnegligible polymer presence in the mixture. Hence there is a jump in chemical potential across the boundary of the gel. It rises rapidly near the boundary, reaching almost immediately its final value, and more slowly inside due to the slow diffusion-like process (Fig.6).

Solvent inhibited through the boundary of the gel either stays near the boundary and inflates this region or diffuses toward the center. Figs.7-8-

 $2 \ 3$

9-10 underline the mechanical properties of the hydrogel and especially the balance between elastic stresses and the pore pressure. The elastic stresses are always and everywhere tensile, because the polymer network has to be stretched in all directions throughout the whole swelling process to leave space for the solvent molecule to flow in the mixture (Figs.7-8). On the one hand, in the free swelling case the fluid volume fraction increases sharply near the boundary leading to the fast growth of the outer pores and to the comparatively slow diffusion of the solvent to the inner regions. Thus, pore expansion near the boundary is dominant over the diffusion towards the central regions, leading to a core-shell structure⁽¹⁶⁾. On the other hand, in the constrained case the same phenomenon is witnessed, with values of the elastic radial and azimuthal stresses slightly higher but of the same order, but the final state is reached at a lower fluid volume fraction, i.e. at a lower swelling ratio due to the presence of the membrane. As the outer part of the gel rapidly reaches its final state in the constrained case, this core-shell structure is less visible and the process is closer to a uniform volumetric expansion. Mechanical balance is ensured by the pore pressure, which grows largely in the constrained case and remains negligible in the free case where the polymer network can be largely stretched and its pores expanded, making room for the newly absorbed solvent. Hence, as the volume of the pores increases, their pressure decreases leading to a comparatively low pore pressure. Whereas in the constrained case, the stiffness of the membrane forces the gel to swell less (the osmotic pressure thus remains nonnegligible) and the pores to remain small (the pore pressure thus becomes large), as expected (Fig.9). In both cases, the gel absorbs solvent molecules due to chemical affinity. Indeed, the study of the decomposition of the chemical potential in terms of osmotic pressure and pore pressure in Eq.(11) shows that the driving phenomena in both cases, even though the increase of the pore pressure in the constrained case helps the diffusion process by adding a mechanical forcing, is the entropic mixing part, i.e. the osmotic pressure (Fig.10). Figs.11-12-13-14 put the emphasis on the

mechanical aspect of the actuation, studying the developed true stresses.

The combination of the two contributions in the Biot's expression of the total stresses in Eq.(11) shows that the latter get highly compressive in the constrained case due to the large pore pressure (Figs. 11-12). On the boundary, the total stress remains equal to 0 in the free swelling case as expected⁽³⁾, with the pore pressure compensating the elastic radial stress. The pore pressure decreases in the free case, as the swelling of the pores occurs. In the constrained case, it sharply becomes compressive as a result of the membrane resistance. This time, the pore pressure increases because the swelling of the pores cannot occur. Both cases show a sharp increase of the elastic radial stress at the beginning of the swelling, when the outer layer is swelling while being stuck to the inner core not yet inhibited, followed by a slow decrease as the inner part becomes swollen (Fig.13). The comparison of the contributions to the total chemical potential of the osmotic pressure and the pore pressure further supports the analysis that the mixing is mainly entropic for both cases (Fig.14).



Fig. 11 Total radial stress σ_r against the non-dimensionalized radius ρ , at various time steps for the free (in blue) and the constrained (in red) cases.



Fig. 12 Total azimuthal stress σ_{θ} against the non-dimensionalized radius ρ , at various time steps for the free (in blue) and the constrained (in red) cases.



Fig. 13 Total radial stress on the boundary $\sigma_r(\rho = 1)$ against time for the free (in blue) and the constrained (in red) cases. Dashed lines are the two components of the total radial stress.



Fig. 14 Normalized chemical potential on the boundary $\tilde{\mu}(\rho = 1)$ against time for the free (in blue) and the constrained (in red) cases. Dashed lines are the two components of the chemical potential.

Chapter 4. Materials and method

4.1. Materials

3-sulfopropyl acrylate potassium salt (SPA; Sigma-Aldrich 251631) and acrylamide (AAm; Sigma-Aldrich A8887) were used as monomers for the core copolymer hydrogel network. N,N'-methylenebisacrylamide (MBAAm; Sigma-Aldrich M7279) and 1-Hydroxy-cyclohexyl-phenyl-ketone (Irgacure 184; Sigma-Aldrich 405612) were respectively used as a cross-linking agent and a photoinitiator. Poly(vinyl alcohol) (PVA, Mw 146,000-186,000, 99+% hydrolyzed; Sigma-Aldrich 363065) and Alginic acid (Alg, medium viscosity; Sigma-Aldrich A2033) were used as monomers for shell hydrogel that is coated onto core hydrogels. Calcium chloride (CaCl2; Sigma-Aldrich C4901) was used to physically crosslink the Alg chain. Ecoflex (00-10; Smooth-On Inc.) was used as a mold for core hydrogel.

Deionized water filtered with a Direct-Q®3 machine (Merck Millipore) was used to make the electrolyte solution. All chemical reagents were used without further purification.

4.2. Fabrication of the hydrogel

Unless otherwise specified, the precursor solution of the core hydrogel P(AAm-co-SPA) was prepared with a molar ratio of 272 : 2727 : 10 : 1 = SPA: AAm: MBAAm: Irgacure 184, where the molar concentration of AAm and SPA monomer were respectively 0.272 M and 2.727 M. The precursor solution was poured into a spherical mold made of Ecoflex, then exposed to 365 nm UV irradiation (CL-1000L UVP) for 10 minutes. The diameter of the core hydrogel sphere was fixed at 5 mm. To fabricate the core-shell hydrogel, first, the coating solution was prepared by dissolving Alg and PVA with a weight ratio of 2 and 3 wt% respectively in deionized water under stirring and heating (90 °C). After degassing by sonication for 1 h, a clear solution was obtained. The core hydrogel that contains multivalent ions can physically crosslink the Alg chain, therefore the core hydrogel was immersed in 3.0 M CaCl2 solution for 1 min and the excess

solution on the surface was completely dried by air blower. Then, the spherical hydrogel was immersed into the coating solution (PVA-Alg) and the pre-gel grows from the surface of the core hydrogel with corresponding coating time. The pre-coated hydrogel was vigorously cleaned with deionized water to remove excessive uncrosslinked polymers. The pre-gel is composed of crosslinked Alg and entangled PVA, so the mechanical strength is very weak to endure the swelling of core-hydrogel. To strengthen the shell hydrogel, the pre-coated hydrogel was annealed in a 120°C oven for 2 hours. The densification of the polymer chain makes the additional hydrogen bonding, which enhances the mechanical properties of the shell. For further enhancement by salting-out, the annealed core-shell hydrogel was immersed into 2.0 M ZnSO4 for 15 min.

4.3. Tensile tests

The square-shaped shell hydrogels were prepared following the above procedure and the pre-gel sheets were cut into dog-bone shaped

33

specimens with a gauge width of 2 mm. The thickness of the individual specimens was varied with coating time and measured with a Vernier caliper. The force-displacement data were obtained using a universal testing machine (1 kN load cell; Instron 3343) at the constant strain rate (10 mm/min). To generate the stress-strain curves, the measured force was divided by the initial gauge cross-sectional area and the measured displacement was divided by the initial clamp distance.

4.4. Compressive tests

The disk-shaped core hydrogels were prepared by using an acrylic mold with a diameter of 10 mm and thickness of 2 mm, followed by UV irradiation for 10 min. The swelling ratios of the specimens were controlled by making the gel swollen in a specific amount of deionized water. The specimens were kept inside a humid chamber for 24 hours to reach the equilibrium state without evaporation. The densities of the hydrogels were obtained by dividing the weight of the measured sample by the volume calculated from the diameter and thickness of the samples. The compressive force-displacement data were obtained using a universal testing machine (1 kN load cell; Instron 3343) at the constant strain rate (1 mm/min). During the tests, the specimens were placed between the stage and load cell filled with mineral oil to prevent evaporation and minimize the friction between the specimens and the load cell. The shear modulus was obtained from the true stress-strain curve where the measured force was divided by the instantaneous cross-sectional area and the measured displacement was divided by the initial thickness.

4.5. Swelling rate measurement

Before measuring the swelling rate of the spherical core-shell hydrogels, the samples were fully dried at room temperature for 1 day. The swelling ratio-time curves were obtained from the diameters of the core-shell hydrogels from the time-lapse images taken by handheld digital microscope (Dinolite AM4815ZT) during the gels swelled in a bath with a large amount of deionized water. The swelling ratio was obtained by dividing the measured diameter at a specific swelling time by the initial diameter of the core-shell hydrogel.

4.6. Validation

We conducted experiments on hydrogel spheres of initial radius a = 2 mm. We first aim at fitting the final swelling ratio for the free swelling case. From our experimental measurements of shear modulus and using Eq.(6) at T = 298 K and I = 32, the number of chains per unit volume of dry polymer is fixed at N = $1.849 \times 10^{25} m^{-3}$ for a shear modulus of G = 23.89 kPa. The value of G is in agreement with usual values from the literature. That of N is roughly one order of magnitude larger than usual values. Indeed, the goal of the present study was not to reach very high swelling ratio and we needed the membrane to withstand the stress induced by the swelling, thus leading to the choice of a denser hydrogel. Hence, the final swelling ratio for the free swelling case now only depends

on χ_0 and χ_1 , which are fitted to match the experimental results. It gives $\chi_0 = 0.49$ and $\chi_1 = 0.04$. We note that the coordination number $z \approx 6$ is reasonable with respects to that of a simple 3D square lattice. We also underline the fact that, even though the expression of the mixing parameter in this study is different with respect to the constant approximation classically used, the value of χ still lies within the generally accepted range 0.49 – 0.51 for polyacrylamide hydrogels, with the value of χ being generally higher in the more constrained case.



Fig. 15 Comparison between experiments averaged over three to four samples (circles) and simulations (full lines).



Fig. 16 Simulated total radial compressive stress produced on the boundary in the same three cases as previously.



Fig. 17 Strain against time in logarithmic scale. Dashed lines underline the power law behaviour at early time and are fitted to the experimental values.

We next consider the final swelling ratio for the constrained swelling case, with membranes of measured initial thickness $h = 250 \ \mu m$. From tensile tests performed on the membranes, we fitted the true stress-stretch curves to the theoretical expression $\sigma_r(\lambda_\theta) = G_m(\lambda_\theta^2 - \lambda_\theta^{-4})$. That way, we computed their shear moduli G_m , which are of the order of the MPa, depending on the membrane.

Lastly the permeability parameter D_0 is fitted to match the time scales of the experiments, which leads to $D_0 = 5.76 \times 10^{-11} m^2/s$. The nondimensionalization step done is conducted using the value of the effective permeability $D = 1.02 \times 10^{-8} m^2/s$ for the free case, which is of the same order of magnitude of values from other studies⁽¹⁵⁻¹⁶⁾, and $D = 4.53 \times$ $10^{-10} m^2/s$ or $D = 3.19 \times 10^{-10} m^2/s$ for the constrained cases. These values correspond to their respective final values, when the mixture has reached its equilibrium state. We note that the value of D increases throughout the swelling process by roughly two orders of magnitude in the free case and only one in the constrained cases. The simulation is then compared to the experimental data, as shown in Fig.15. We obtain a satisfying fit both in terms of prediction of the final swelling ratio and prediction of the kinetics of the two processes. The theoretical model then allow use to compute the actuating pressure inside of the gel. As expected, the more constrained the gel is, the larger internal pressure it builds. The negative values of σ_r indicate that the stress is compressive (Fig.16). In all cases, at early times the power law behaviour resembles that of a diffusive process with an exponent close to 0.5. The seemingly increasing exponent (with respect to the constraint) may be purely artificial, as the fitting to a power law seems to get less and less relevant as the gel gets more constrained (Fig.17).

Conclusion

We studied the kinetics of swelling of constrained hydrogel spheres using a thermodynamic approach based on the theory of Hong *et al.* After having built the theoretical framework, we used it to perform simulations and understand in more depth the swelling process. To validate the simulations, we conducted free and constrained swelling experiments with two different membranes. Using experimentally measured, fixed, or fitted parameters, we simulated the process and it matched satisfactorily well the experimental results. This work aims at helping the design of future soft actuators by understanding the behavior and the role of the different aspects of the swelling process.

Bibliography

- (1) D. J. Beebe, J. S. Moore, J. M. Bauer, Q. Yu, R. H. Liu, C. Devadoss and B.-H. Jo, 2000, "Functional hydrogel structures for autonomous flow control inside microfluidic channels", Nature, Vol. 404, No. 6778, pp. 588~590.
- (2) R. Bashir, J. Z. Hilt, O. Elibol, A. Gupta and N. A. Peppas, 2002, "Micromechanical cantilever as an ultrasensitive pH microsensor", Applied Physics Letters, Vol. 81, No. 16, pp. 3091~3093.
- (3) H. Na, Y.-W. Kang, C. S. Park, S. Jung, H.-Y. Kim and J.-Y. Sun, 2022, "Hydrogel-based strong and fast actuators by electroosmotic turgor pressure", Science, Vol. 376, No. 6590, pp. 301~307.
- (4) A. Jain, Y.-T. Kim, R. J. McKeon and R. V. Bellamkonda, 2006, "In situ gelling hydrogels for conformal repair of spinal cord defects, and local delivery of BDNF after spinal cord injury", Biomaterials, Vol. 27, No. 3, pp. 497~504.
- (5) Y. Xiao, W. Xu, Q. Zhu, B. Yan, D. Yang, J. Yang, X. He, S. Liang and X. Hu, 2009, "Preparation and characterization of a novel pachyman-based pharmaceutical aid. II: A pH-sensitive, biodegradable and biocompatible hydrogel for controlled release of protein drugs", Carbohydrate Polymers, Vol. 77, No. 3, pp. 612~620.
- (6) M. Bassil, J. Davenas and M. EL Tahchi, 2008, "Electrochemical properties and actuation mechanisms of polyacrylamide hydrogel for artificial muscle application", Sensors and Actuators B: Chemical, Vol. 134, No. 2, pp. 496~501.
- (7) K. Deligkaris, T. S. Tadele, W. Olthuis and A. van den Berg,

2010, "Hydrogel-based devices for biomedical applications", Sensors and Actuators B: Chemical, Vol. 147, No. 2, pp. 765~774.

- (8) T. Tanaka, L. O. Hocker and G. B. Benedek, 1973, "Spectrum of light scattered from a viscoelastic gel", The Journal of Chemical Physics, Vol. 59, No. 9, pp. 5151~5159.
- (9) T. Tanaka and D. J. Fillmore, 1979, "Kinetics of swelling of gels", The Journal of Chemical Physics, Vol. 70, No. 3, pp. 1214~1218.
- (10) T. Komori and R. Sakamoto, 1989, "On Tanaka-Fillmore's kinetics swelling of gels", Colloid and Polymer Science, Vol. 267, No. 2, pp. 179~183.
- (11)W. Hong, X. Zhao, J. Zhou and Z. Suo, 2008, "A theory of coupled diffusion and large deformation in polymeric gels", Journal of the Mechanics and Physics of Solids, Vol. 56, No. 5, pp. 1779~1793.
- (12) P. J. Flory, 1942, "Thermodynamics of High Polymer Solutions", The Journal of Chemical Physics, Vo. 10, No. 1, pp. 51~61.
- (13)M. L. Huggins, 1941, "Solutions of Long Chain Compounds", The Journal of Chemical Physics, Vol. 9, No. 5, pp. 440~440.
- (14)C. A. Grattoni, H. H. Al-Sharji, C. Yang, A. H. Muggeridge and R. W. Zimmerman, 2001, "Rheology and Permeability of Crosslinked Polyacrylamide Gel", Journal of Colloid and Interface Science, Vol. 240, No. 2, pp. 601~607.
- (15) M. Engelsberg and W. Barros, 2013, "Free-evolution kinetics in a high-swelling polymeric hydrogel", Physical review. E, Statistical, nonlinear, and soft matter physics, Vol. 88, No. 6, pp. 062602.
- (16) T. Bertrand, J. Peixinho, S. Mukhopadhyay and C. W. MacMinn, 2016, "Dynamics of Swelling and Drying in a

Spherical Gel", Physical Review Applied, Vol. 6, No. 6, pp. 064010.

Abstract in Korean

용매에 담근 가교 폴리머 네트워크는 주변 분자를 흡수하여 일시적인 팽 창을 일으킵니다. 엔트로피에 의한 혼합 거동으로 인해 용매 분자가 네 트워크 내에서 흐르고 기공을 채우면서 기공 압력이 증가합니다. 그런 다음 네트워크가 늘어나서 기공의 크기가 커지고 더 많은 용매가 안쪽으 로 흐르게 됩니다. 젤의 투과성은 모공의 크기에 따라 증가하여 팽창 과 정의 동역학에 영향을 미칩니다. 에너지적으로 유리한 혼합과 에너지적 으로 불리한 연신 사이에 평형에 도달하면 팽창이 멈춥니다. 반투과성 멤브레인의 제약 하에서 시스템은 덜 팽창하고 그 대가로 더 큰 내부 압 력을 증가시킵니다. 제약된 성장에 대한 이론적 분석은 지금까지 존재하 지 않았습니다. 우리는 비선형 포로엘라스틱 이론을 사용하여 제약 조건 하에서 팽창의 동역학을 모델링하고 시뮬레이션 결과가 3-설포프로필 아 크릴산 칼륨 염과 아크릴아마이드의 혼합물로 만든 하이드로젤 비드의 실험 데이터와 잘 일치한다는 것을 발견했습니다. 제한된 하이드로젤이 팽창하는 동안 발생하는 응답 시간과 작동 응력을 이해하고 예측하면 폴 리머 기반 소프트 액추에이터를 설계하는 데 도움이 됩니다.

4 6